

# PATENT SPECIFICATION

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## (54) POURABLE MARGARINE OF THE WATER-IN-OIL EMULSION TYPE

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to pourable phosphatide-containing emulsions having improved stability against oil separation. In particular the invention relates to pourable margarines of the water-in-oil type and to a process for the preparation thereof. Pourable margarines, which are mainly of importance for frying purposes should contain phosphatide or derivatives thereof to improve the spattering characteristics.

Conventional margarine is usually plastic at ambient temperature. This plasticity is mainly attributable to the nature of the fatty phase of the water-in-oil emulsion constituting margarine, in particular to the presence of substantial proportions of fatty matter which exist in the solid state at ambient temperature, but also to a great extent to the presence of emulsifiers in the fatty phase.

It is generally accepted that the glyceride crystals of the fatty matter in plastic margarines are present as a three-dimensional solid network in which liquid oils and droplets of the aqueous phase are enclosed and this arrangement forms an important contribution to the stability of such margarines against oil separation.

Attempts have been made to prepare phosphatide-containing margarines which are pourable at ambient temperature and preferably also at refrigeration temperatures, but which are nevertheless similarly stable against oil separation. The requirement for pourability, however, sets a limit to the amount of hard fat that can be incorporated in such compositions. While the maximum hard-fat content in the fatty phase in pourable margarine is dependent on several factors, e.g. the viscosity

of the margarine required at storage and use conditions, the type, melting point and particle size of the hard-fat component used and the process conditions under which the product is prepared, it is generally found that neither the maximum allowable amount of hard-fat nor the presence of the best edible emulsifiers available in the fatty phase, is adequate to arrive at a product which is sufficiently stable against oil separation, especially at relatively high use temperatures, e.g. 20° to 35°C.

The pourable phosphatide-containing margarines therefore generally contain less hard-fat than would be necessary to stabilize the emulsion adequately against oil separation.

It has now been found that the stability against oil separation of a pourable phosphatide-containing margarine of the water-in-oil type can be improved by incorporating a phosphatide in the aqueous phase, of which phosphatide from 5—35% by weight is a monoacylglycerophosphatide whose acyl group is derived from a fatty acid having at least 12 carbon atoms. The pourable margarines of the invention can contain any convenient ingredient for such products and 0.5 to 4% by weight of said monoglycerophosphatide in the aqueous phase.

It is a great advantage of the products of the invention that they are not only excellently stable against oil separation at temperatures of up to 35°C, but that they also show a significant reduction in spattering behaviour during frying.

Monoacylglycerophosphatides lack one of either the  $\alpha$ - or  $\beta$ - acyl groups of diacylglycerophosphatides, and typical of them are  $\alpha$ - and  $\beta$ -lysolecithin and  $\alpha$ - and  $\beta$ -lysocephalin. Monoacylglycerophosphatides can be prepared by synthesis or they can be obtained by the chemical hydrolysis (see e.g. British patent application No. 18163/68) Specification No. 1,229,430 or the enzymatic partial hydrolysis of diacylglycerophosphatides.  $\alpha$ -Monoacylglycerophosphatides can be prepared by

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the action on diacylglycerophosphatides of the enzyme phospholipase A (lecithinase A), which is conveniently prepared free of other enzymes by the partial heat inactivation of pancreatin. For this aqueous suspension of pancreatin can be heated to from 70° to 80°C for 30 minutes or to 90°C for 10 minutes. The phosphatide used for the hydrolysis can be a phosphatide slime obtained in the production of plant oils, for example soybean oil or rapeseed oil, and steam or water treatment of the extracted oils at 95°C to 100°C, or the crude phosphatide obtained by centrifuging such a phosphatide slime and drying the product under reduced pressure: a typical crude phosphatide thus obtained contains about 65% diacylglycerophosphatides and 35% oil.

In preparing  $\alpha$ -monoacylglycerophosphatide by enzymatic hydrolysis of such a phosphatide the latter is dissolved or suspended in water, or a solvent containing sufficient water, with from 0.1 to 25% of heat-treated pancreatin by weight of the phosphatide, and hydrolysis allowed to proceed at ambient temperature until a sufficient concentration of the monoacyl compound has been formed. Preferably the water contains calcium ions and tap water of 5 to 30° hardness is suitable. Fatty acid produced and contaminating fat can subsequently be removed by drying the product, for instance by evaporation under reduced pressure, and extracting it with acetone. A phosphatide containing from 5 to 45% of monoacylglycerophosphatide, depending on the degree of hydrolysis effected, can be obtained in this way. Only those products containing 5–35%, preferably 10–25% monoacylglycerophosphatide, are suitable for the purpose of the invention. The amount of monoacylglycerophosphatide in the product of hydrolysis can be determined by standard analytical methods, for instance thin-layer chromatography.

In practice the fatty acid acyl group of the monoacylglycerophosphatide has from 12 to 24 carbon atoms, and the monoacylglycerophosphatide produced from a natural phosphatide will generally have its monoacyl group derived from mixed fatty acids, especially those of 16 to 22 carbon atoms. Preferably the monoacylglycerophosphatide comprises lysolecithin and lysocephalin.

In preparing the pourable margarines sufficient monoacylglycerophosphatide is incorporated in the aqueous phase to obtain the stability required: preferably the amount used is within the range of from 1 to 3.5% by weight of the aqueous phase.

Pourable margarines may be prepared from a fatty phase, the greater part of which, preferably at least 60%, is composed of a glyceride oil remaining pourable at temperatures from 5 to 35°C. it can contain a small amount of fatty acid monoglyceride, e.g. from 0.05 to 0.5% of the fatty phase. It is pre-

ferred that the pourable margarines are prepared from a fatty phase containing 90 to 99.5% of an oil which is liquid at temperatures from 0° to 35°C.

Margarines containing a high content of polyunsaturated fatty acids, notably those known as essential fatty acids, are nowadays of particular interest since these products are widely believed to be dietetically beneficial.

It is therefore preferred that liquid vegetable oils containing at least 40% of polyunsaturated fatty acids are used for this purpose, e.g. sunflower, safflower, soybean, wheat germ, rapeseed, poppyseed, tobacco seed, rye, walnut or corn oil.

The amount of the hard-fat component present in the pourable margarine of the invention may vary, e.g. up to about 10%, depending on the type and melting point of the hard-fat used and the process in which the emulsion is prepared.

Preferably substantially saturated hard-fat components are used, which components may, for instance, be obtained by substantially completely hydrogenating a vegetable or animal oil.

Preferably from 1 to 5%, based on the total amount of the fatty phase, of a substantially saturated hard-fat component is used, e.g. substantially completely hydrogenated rapeseed oil, mustard seed oil, groundnut oil, soybean oil, sunflower oil, lard, tallow, palm oil or cottonseed oil.

The particle size of the hard-fat particles present in the pourable emulsion is also of importance. Hard-fat of which at least 90% of the particles have a major dimension of from 0.1 to 30 microns, preferably from 0.1 to 5 microns, is excellently suitable for the purpose of the invention.

Excellent pourable margarines have been prepared containing in their fatty phase sunflower oil and from 1 to 4%, preferably 1 to 2% of fully hydrogenated rapeseed oil having a melting point of from 55 to 75°C and an aqueous phase comprising water and/or soured skim milk together with a minor amount of monoacylglycerophosphatides.

The pourable emulsions of the present invention may be used for the preparation of foodstuffs, e.g. soups, sauces, stews, gratinated dishes and sandwiches, and especially for frying and baking purposes.

The product of the invention may be prepared by conventional margarine preparative techniques, for example by the use of scraped-surface heat exchangers, such as Votators ("Votator" is a registered Trade Mark). In such apparatus the blend of oil phase and aqueous phase, including such additives as are customary in the preparation of margarine, for example flavouring agents and colouring matter, are simultaneously blended and chilled, e.g. to from 0°C to 20°C. Further details of this preparative method appear in

"Margarine" by Andersen & Williams, Pergamon Press, London, 1954, pages 228 et seq.

In a preferred process of the invention a pourable margarine is prepared by emulsifying the liquid fatty phase with an aqueous dispersion of the monoacylglycerophosphatide-containing phosphatide to produce the water-in-oil emulsion. The aqueous dispersion can be made by mixing the phosphatide containing monoacylglycerophosphatide with the remainder of the aqueous phase, for instance skim milk, and heating if necessary. This emulsion may subsequently be cooled to a temperature of from 0° to 20°C, filled into receptacles and subsequently stored for 5 to 50 hrs at a temperature of from 5° to 18°C.

As the emulsifying properties of monoacylglycerophosphatides are less affected by alkaline earth metal ions than diacylglycerophosphatides, it is possible to use hard water or calcium-containing protein solutions without the addition of complex-forming salts or acids. Moreover the aqueous phase can contain up to 10% of salt.

For margarine an acid pH is preferable on bacteriological grounds. The aqueous phase or the emulsion formed can be made acid to the required pH with lactic, citric, or other suitable acid, or by the action of bacteria, for instance with the addition of 0.5 to 1% of lactic acid culture where the appropriate bacterial substrate is present. Preferably the pH of the emulsion is from 4 to 5.

The invention is illustrated by the following Examples:

#### EXAMPLE I.

100 g of commercially available crude soya phosphatide (65% phosphatides, 35% oil) was vigorously stirred to an emulsion with 80 ml water and 20 ml of a suspension of 0.5% pancreatin in water. The mixture was stirred for 20 hours at 55°C, after which the acid value calculated on the water-free product had increased from about 20 to 36. The aqueous suspension was dried under vacuum at 60°C. A partially hydrolysed phosphatide product was obtained having an  $\alpha$ -monoacylphosphatide content of about 12%.

To a mixture of tap water (260 g) of 12° G.H. and skim milk (140 g) a partially hydrolysed phosphatide was added (10 g).

To disperse the phosphatides at room tem-

perature the pH of the water phase was brought with lye at 9. After the dispersing of the phosphatides the pH was reduced to 4.7 with the aid of lactic acid. The aqueous phase had a milky appearance and no flocculation of phosphatides could be observed. The aqueous phase obtained was dispersed in a refined fat phase (2000 g) which was brought at 42°C and which consisted of 98.5% sunflower oil and 1.5% fully hydrogenated rape oil with a slip melting point of 70°C. To this fat phase also 0.2% monoglycerides were added together with small quantities of colouring oil and flavours. The sunflower oil contained about 60% linoleic acid calculated on the total quantity fatty acids and it remained clear and pourable at -5°C and higher temperatures. The water-in-oil emulsion was cooled with a laboratory Votator A-unit (Votator is a registered Trade mark) to 4°C and thereafter the cooled emulsion was worked in a conventional stirred crystallizer unit and filled into plastic bottles.

The oil exudation of a sample of the liquid margarine obtained was assessed after the margarine had been kept at 30°C. for 3 weeks in a glass cylinder with a diameter of 3.7 cm and a volume of 250 ml. The cylinder was filled to a height of 10 cm. The oil exudation was expressed in % of the margarine sample. This was compared with the results of a control sample which contained the same ingredients but of which the phosphatides were dispersed in the fatty phase. Also the spattering behaviour on frying was compared with the aid of the following test:

In an enamelled pan with smooth bottom surface each time 50 g margarine were fried at 175°C (controlled with a thermo-couple). At a distance of 21 cm above the pan the fat spattering away was caught on a piece of paper which had been weighed before.

After the test the paper was weighed again. The weight increase of the paper was a measure for the degree of spattering and was converted into a score as follows:

10 (very good) : less than 10 mg  
6 (moderate) : 50 to 100 mg  
2 (very bad) : > 500 mg

Intermediate scores express a corresponding spattering behaviour.

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The results were:

	Oil exudation 30°C	Spattering test
Liquid margarine according to the invention	2.5%	8—9
Control	18.5%	8—8

These results show that by incorporation of monoacylglycerophosphatides in the aqueous phase instead of in the fatty phase of a pourable margarine, a significant improvement in stability is obtained without detrimentally affecting its spattering properties.

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These liquid margarines were prepared as described in Example I, using the same ingredients, except that the proportions of fully hydrogenated rapeseed oil and monoacylglycerophosphatide were varied.

The three margarines thus prepared were compared with three margarines prepared from the same ingredients, except that unhydrolysed phosphatide was used as emulsifier in the aqueous phase.

The results are shown in Table I.

#### EXAMPLES II—IV.

Three liquid margarines were prepared as described in Example I, using the same in-

TABLE I

Ex. No.	Liquid oil (%)	Hard fat (%)	Enzymatically hydrolysed phosphatide in aqueous phase (%)	Unhydrolysed phosphatide in aqueous phase (%)	Water distribution, number of droplets per 0.01 mm <sup>2</sup>				Spattering test	Oil separation after 3 weeks at 30°C (%)
					>24μ	12—24μ	6—12μ	3—6μ		
2	98.5	1.5	1.8	—	4	61	1460	5600	7.5—7	6
Control	98.5	1.5	—	1.8	0	37	1000	6460	0 —0	10
3	98.5	1.5	3.0	—	0	7	930	7900	7.5—7	5
Control	98.5	1.5	—	3.0	0	5	900	5700	3.5—4	26
4	99.0	1.0	3.0	—	0	25	1350	7000	8 —8	16
Control	99.0	1.0	—	3.0	2.5	72	1800	8000	4 —3.5	50

From the results of the experiments of Table I it is to be concluded that by incorporating monoacylglycerophosphatides in the aqueous phase of a pourable margarine not only the stability against phase separation but also the spattering behaviour is significantly improved as compared with the stability and spattering behaviour of pourable margarines prepared with unhydrolysed phosphatide in the aqueous phase.

#### EXAMPLES V—VIII.

Three liquid margarines were prepared as described in Example III and Table I, except that the degree of hydrolysis of the phosphatides and thus the percentage of monoacylglycerophosphatide in the phosphatide mixture was varied.

The results are shown in Table II.

TABLE II

Example No.	% monoacylglycerophosphatide in the phosphatide mixture	% oil separation after storage at 30°C			spattering test
		1 week	2 weeks	3 weeks	
control (see also Table I)	0	7	12	26	4
5	8	3	4	9	6.8
6	15	4	6	8	8.2
7	30	3	3	6	6.8
control	40	4	4	6	5.2

From the results of the experiments compiled in Table II it follows that pourable margarines containing phosphatide in the aqueous phase, from 5—35% by weight of which phosphatides are monoacylglycerophosphatides, are excellently stable against oil separation at 30°C and possess good frying properties.

#### WHAT WE CLAIM IS:—

1. A pourable margarine of the water-in-oil emulsion type, comprising a phosphatide in the aqueous phase from 5 to 35% by weight of which phosphatide is a monoacylglycerophosphatide whose acyl group is derived from a fatty acid having at least 12 carbon atoms.
2. A margarine according to Claim 1, in which 10—25% of the phosphatide is the monoacylglycerophosphatide.
3. A margarine according to Claim 1 or 2, in which the acyl group of the monoacylglycerophosphatide has from 16—22 carbon atoms.
4. A margarine according to Claims 1—3, in which the monoacylglycerophosphatide is an alpha-monoglycerophosphatide.
5. A margarine according to Claim 4, in which the monoacylglycerophosphatide comprises lysolecithin.
6. A margarine according to any of Claims 4—5, in which the monoacylglycerophospha-

tide is one that has been obtained by the action of phospholipase A on diacylglycerophosphatide.

7. A margarine according to Claim 6, where the phospholipase A used was obtained by partial heat inactivation of pancreatin.

8. A margarine according to Claim 6 or 7, where the diacylglycerophosphatide used was a soybean phosphatide.

9. A margarine according to any preceding claim, wherein the major amount of the fat phase is a glyceride oil remaining pourable at temperatures from 5°C to 35°C.

10. A margarine according to Claim 9, in which at least 60% of the fatty phase is an oil pourable at temperatures between 5° and 35°C.

11. A margarine according to Claim 9 or 10, in which from 92—99.5% by weight of the fatty phase is an oil which is pourable at temperatures between 0° and 35°C.

12. A margarine according to Claims 9—11, in which the fatty phase comprises a liquid vegetable oil at least 40% by weight of its fatty acids being polyunsaturated fatty acids.

13. A margarine according to Claim 12, in which the liquid vegetable oil comprises safflower, sunflower, soybean, wheat germ, grape-seed, poppyseed, tobacco seed, rye, walnut or corn oil.

14. A margarine according to any of the preceding claims in which the fatty phase

comprises a substantially saturated hard-fat component as stabilizing agent.

5 15. A margarine according to Claim 14, in which the fatty phase comprises from 1—5% of the hard-fat component.

16. A margarine according to Claims 14 and 15, in which at least 90% of the particles of the hard-fat have a major dimension of 0.1—5 $\mu$ .

10 17. A margarine according to any of the preceding claims containing from 0.5 to 4% of monoacylglycerophosphatide by weight of the aqueous phase.

15 18. A margarine substantially as described in any one of the Examples.

19. Foodstuffs comprising or prepared with the margarine as described in any of the preceding claims.

20 20. A process for preparing a pourable, stable margarine according to any preceding claim, which comprises dispersing a phos-

phatide containing aqueous phase in a liquid fat phase, from 5—35% by weight of which phosphatide being monoacylglycerophosphatide.

25 21. Process according to Claim 20, which comprises emulsifying the aqueous phase into the molten fat phase, cooling the emulsion to a temperature of from 0° to 20°C, filling the cooled emulsion into receptacles and storing the filled receptacles for 5 to 50 hrs at a temperature of from 5° to 18°C.

30 22. Process for the preparation of foodstuffs, which comprises incorporating therein a substantial amount of the pourable margarine as claimed in any of Claims 1—19 or prepared according to Claims 20—21.

35 23. A margarine prepared according to any of Claims 20—22.

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